

REMARKS

Claims 1, 4 and 5 were rejected under 35 U.S.C. § 102 for lack of novelty, or alternatively, under 35 U.S.C. § 103 for obviousness predicated upon Harris et al., Sugiura et al. and Japanese Document 08157265 (JP '265), each taken alone.

Claims 1, 4 and 5 were also rejected under 35 U.S.C. § 102 for lack of novelty, or alternatively, under 35 U.S.C. § 103 for obviousness predicated upon Japanese Document 5-229873 (JP '873).

Each of the above rejections is traversed.

Independent claim 1 is directed to an aluminum nitride ceramic base material exhibiting **specific properties**, i.e., an increment in warp after a single heat treatment at 850°C for one hour of not more than 2.0×10^{-2} $\mu\text{m}/\text{mm}$, and a specified uniform distribution of sintering agents. As previously argued of record, none of the applied references discloses or suggests an aluminum nitride ceramic base material as claimed having the recited uniformity of sintering agents and increment in warp. Indeed, none of the applied references recognizes, discloses, or addresses the **problem of increment in warp after heat treatment**, let alone recognizes that it is **related** in any way to the uniformity of sintering agents (a/b), as specifically recited in independent claim 1.

Applicants stress that none of the applied references even discloses or recognizes that the warpage of an aluminum nitride ceramic increases with heat treatment, as disclosed in the present Application. The applied references do not mention or recognize that the fluorescent X-ray-peak strengths of the sintering agents on the top side and the bottom side of the base material impact warpage. The applied references neither disclose nor suggest that the sintering agent is uniformly distributed in the aluminum nitride base material.

The above argued deficiencies in each of the applied references are not overcome by invoking the doctrine of inherency. As argued throughout prosecution of this Application, inherency requires **certainty**, not speculation. *Crown Operations International Ltd. v. Solutia Inc.*, 289 F.3d 1367, 62 USPQ2d 1917 (Fed. Cir. 2002); *Finnegan Corp. v. ITC*, 180 F.3d 1354, 51 USPQ2d 1001 (Fed. Cir. 1999); *In re Robertson*, 169 F.3d 743, 49 USPQ2d 1949 (Fed. Cir. 1999); *Electro Medical Systems S.A. v. Cooper Life Sciences, Inc.*, 34 F.3d 1048, 32 USPQ2d 1017 (Fed. Cir. 1994); *In re Rijckaert*, 9 F.3d 1531, 28 USPQ2d 1955 (Fed. Cir. 1993); *Continental Can Co. USA, Inc. v. Monsanto Co.*, 948 F.2d 1264, 20 USPQ2d 1746 (Fed. Cir. 1991). Simply put, there is an insufficient factual basis upon which to invoke the doctrine of inherency.

In this respect, Applicants would note that in the method disclosed by Sugiura et al., sintering is executed by inserting boron nitride (BN) powder between formed bodies (degassed bodies) in a stacked state. In this manner the formed bodies are prevented from mutual adhesion during sintering. It is estimated that there is no difference the concentration of the sintering agents among the stacked formed bodies except for the uppermost one. However, since the sintered substrates **are warped**, an unwarping is executed. In case of such warping during sintering, for example when the first body is warped in a convex form and the second body is warped in a concave form, it is anticipated that the sintering agent is present in a relatively small amount between the mutually opposed faces of the first and second bodies, possibly causing a diffusion to the ambient atmosphere. On the other hand, when the first body is warped in a concave form and the second body is warped in a convex form, it is anticipated that the concentration of the sintering agent is higher between the mutually opposed faces. Clearly,

Sugiura et al. neither disclose nor suggest the notion of sintering with a uniform concentration of sintering agents, as in the claimed invention.

The remaining applied references are no more relevant than Sugiura et al. The notion of implementing sintering with the uniform distribution of sintering agents as in the claimed invention, let alone the impact of such uniformity on warpage, is not even a blip on the radar screens of any of the applied references.

It should be noted that paragraph [0014] of the present Application discloses “a sheet formed by a porous nitride ceramics such as boron nitride (BN).” Paragraph [0022] describes that “setters of samples 10-17 were prepared by sintering a formed body made of the powder material at 1800°C in nitrogen”. The setters of samples 10-17 are formed by BN. Although there is no specific description as to whether a body formed by sintering BN at 1800°C is porous, one having ordinary skill in the art would have understood that a body sintered at 1800°C would be porous. For example Japanese Patent No. 2614874 discloses that BN sintered at 1800-2100°C has a relative density of 65-80%, which is manifestly porous. A copy of Japanese Patent No. 2614874 published on May 28, 1997 and a computer translated copy thereof, are submitted herewith as Exhibit A.

Based upon the foregoing it should be apparent that the imposed rejections do not rest upon a sound factual foundation. Moreover, as argued throughout the prosecution, there is evidence of record undermining the inherency theory. Specifically, advertent to Table 2 on page 20 of the written description of the specification, each and every sample in accordance with the present invention, heat-treated at 850°C for one hour, and having a uniformity of sintering agents a/b less than or equal to 1.3, as specifically recited in claim 1, **exhibited an increment in warp after a single heat treatment of no greater than 2.0×10^{-2} um/mm**. However, comparative

examples 22 through 25 exhibited an increment in warp greater than that specified in claim 1, and these samples had a ratio a/b greater than 1.3. While comparative examples 28 and 29 had a low increment in warp, the samples exhibited totally unsatisfactory warp after sintering. **Again, the applied prior art is oblivious to the problem of increment in warp after heat treatment.**

The data clearly establish that the reduced increment in warp after heat treatment at 850°C for one hour, as specified in independent claim 1, does **not just happen by chance**, as evidenced by comparative example 22, 23, 24 and 25. Neither does the advantageously low warp after sintering. Rather, Applicants **discovered** that the reduced increment in warp after heat treating and as well as warp after sintering are linked to the uniformity of sintering agents as specified in independent claim 1. **These unrecognized features are specified in independent claim 1, i.e., claim 1 specifies the ratio a/b and quantifies the maximum increment in warp after a particular heat treatment at 850°C for one hour.**

Applicants again stress that the increment in warp after heat treatment is **not a problem recognized** by any of the applied references. Neither is the significance of the uniformity of sintering agents. Clearly, none of the applied references recognizes any relationship between the uniformity of sintering agents and increment in warp. The possibility that one having ordinary skill in the art might inadvertently **stumble** into the claimed invention is **not** a basis for defeating the patentability of the claimed invention. *W. L. Gore & Associates, Inc. v. Garlock, Inc.*, 721 F.2d 1540, 220 USPQ 303 (Fed. Cir. 1983); *In re Oelrich*, 666 F.2d 578, 212 USPQ 323 (CCPA 1981).

Based upon the foregoing it should be apparent that a *prima facie* basis to deny patentability to the claimed invention under 35 U.S.C. § 102 has not been established for lack of the requisite factual basis. Moreover, there is no factual basis upon which to predicate the

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conclusion that one having ordinary skill in the art would have been realistically motivated to modify any of the articles disclosed in the applied references to arrive at the claimed invention absent, of course, improper reliance upon Applicants' disclosure. *Panduit Corp. v. Dennison Mfg. Co.*, 774 F.2d 1082, 227 USPQ 337 (Fed. Cir. 1985).

Applicants, therefore, submit that the imposed rejection of claims 1, 4 and 5 under 35 U.S.C. § 102 for lack of novelty, or alternatively, under 35 U.S.C. § 103 for obviousness predicated upon Harris et al., Sugiura et al., JP '265 and JP '873, each considered alone, is not factually or legally viable and, hence, solicit withdrawal thereof.

Based upon the foregoing it should be apparent that the imposed rejections are not viable, and that all pending claims are in condition for immediate allowance. Favorable consideration is, therefore, solicited.

To the extent necessary, a petition for an extension of time under 37 C.F.R. 1.136 is hereby made. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to Deposit Account 500417 and please credit any excess fees to such deposit account.

Respectfully submitted,

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EXHIBIT A

* NOTICES *

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CLAIMS

(57) [Claim(s)]

[Claim 1] The insulation resistance of 1010ohms or more, the ordinary pressure sintering boron nitride Plastic solid thermal conductivity 0.04 cal/cm-sec and more than ** which come to contain alkaline-earth-metal borate two to 40% of the weight, and are characterized by being the relative density of 65 - 80%, and the bending strength of 550kg/cm² or more.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

<Field of the Invention> This invention relates to an ordinary pressure sintering boron nitride Plastic solid.

<Prior art> While boron nitride (BN) has the outstanding properties, such as electric insulation, thermal conductivity, corrosion resistance, thermal shock resistance, and lubricity, it is one of a few easy ceramics of machining. For this reason, it is widely used for the electrical insulation material, the elevated-temperature heat transfer ingredient, etc. including the various containers for metal melting with which many above-mentioned properties are demanded.

since BN of BN sintered compact is a difficulty degree of sintering -- general -- a hotpress (pressure sintering) -- it is made by law. Since it is what puts on which and carries out the pressure exceeding 100kg/cm² at 1500-2300 degrees C, a large-scale configuration article is not obtained and a not suitable problem has it in the process of a complicated configuration article. And since the approach of once machining the sintered compact by which the hotpress was carried out to the shape of a cylinder, and making a final product configuration is taken, BN Plastic solid by which current marketing is carried out is an expensive rank.

Although various kinds of ordinary pressure sintering processes are tried in order to solve the above problems, BN sintered compact which can demonstrate the property of BN is not obtained the place which it is till the present. For example, in JP,61-132563,A, production efficiency is bad the top where a consistency and reinforcement are [that sintering in the bottom which inserts in graphite mold the preforming object by which high-pressure rubber press shaping might be carried out, and restricts free expansion is tried] low, and there is a problem from which a large-scale configuration article is not obtained. Therefore, it has the property which was excellent in BN original, such as electric insulation, heat transfer nature, corrosion resistance, and thermal shock resistance, and offer of the ordinary pressure sintering BN Plastic solid which can be manufactured easily and efficiently cheaply was desired.

<Trouble which invention tends to solve> This invention aims at offering the good ordinary pressure sintering BN Plastic solid of thermal conductivity and electric insulation which has improved configuration constraint and productivity of BN sintered compact, and was not acquired conventionally.

<Means for solving a trouble> That is, this invention is an ordinary pressure sintering boron nitride Plastic solid thermal conductivity 0.04 cal/cm-sec and more than the insulation resistance of 1010ohms or more, and ** which comes to contain alkaline-earth-metal borate two to 40% of the weight, and is characterized by being the relative density of 85 - 80%, and the bending strength of 550kg/cm² or more.

This invention is explained to a detail below.

In a commercial item, although BN powder used by this invention is good, it is desirable crystalline hexagonal high BN powder. Since this powder is excellent in the plastic deformans at the time of preforming, the preforming object of high density is easy to be acquired. As an alkaline earth metal of an alkaline-earth-metal boron salt, one or more sorts of magnesium, calcium, strontium, and barium are chosen as arbitration.

How to calcinate, after fabricating the mixed powder mixed so that the Plastic solid of this

invention might become a final product presentation about the above BN powder and alkaline-earth-metal borate by the two or more 5 ton/cm pressure. The mixture of BN and alkaline-earth-metal borate until it mixes alkaline-earth-metal borate to BN powder which it comes to pulverize until it becomes that [twice / more than / which received specific surface area] or specific surface area becomes twice [more than] origin And fracture, It can manufacture by the approach of calcinating, after grinding shear, grinding, etc. and fabricating by the two or more 2 ton/cm pressure.

As shaping equipment, the usual making machines, such as a metal mold making machine and an isotropic pressure making machine (CIP) between the colds, can be used. The compacting pressure when using crystalline hexagonal high BN powder or crystalline amorphous BN powder as it is is two or more 7 ton/cm preferably two or more 5 ton/cm. In less than two 5 ton/cm compacting pressure, it becomes difficult to acquire the ordinary pressure sintering BN Plastic solid of 65% or more of relative density. The effectiveness as the above that the compacting pressure when using the powder which, on the other hand, mixed and pulverized pulverized BN powder or the raw material which came to hand is the same at two or more 2 ton/cm is acquired. As grinding equipment at this time, the usual grinders, such as a ball mill, a vibration ball mill, attritor, and a RAIKAI machine, can be used. In addition, grinding is performed until it becomes 10 or more times twice [more than] as preferably as the specific surface area of the original powder. In grinding of under 2 double, it becomes difficult to acquire the ordinary pressure sintering BN Plastic solid of 65% or more of relative density.

When grinding, if it is performed by the oxidizing atmosphere, generation of a boron oxide will be seen, if it calcinates as it is, it not only causes decline in moisture resistance and thermal conductivity, but it will be in the condition that the oxidation boric acid of isolation exists in a sintered compact, and a crack will occur in a sintered compact. In this case, it can be used as a raw material which obtains this invention article by performing processing which removes the generated boric acid oxide. As an approach of removing a boron oxide, it is processing by alcohols, such as a methanol, ethanol, and a glycerol. Specifically, they are ***** washing and filtration at heating or alcohol containing alcohol of a slurry. A device to which a boron oxide does not generate grinding and which will remove the above-mentioned boron oxide if it carries out, for example by non-oxidizing atmospheres, such as N₂ and Ar, is not necessarily required. What ground by the above-mentioned approach can acquire the ordinary pressure sintering BN Plastic solid of 65% or more of relative density, without carrying out high-pressure molding. This is considered because it became the powder which the newly formed granular structure appeared and was activated by the so-called mechanochemical effect at the same time the stacking fault of a crystal and partial amorphous-ization progress. In order to acquire the ordinary pressure sintering BN Plastic solid of high intensity, it is desirable to make compacting pressure high and to make preforming volume density as high as possible.

Baking is performed by the 1400-2100-degree C non-oxidizing atmosphere. Since burning temperature cannot join alkaline-earth-metal borate to BN grain comrade and BN grain easily directly at less than 1400 degrees C, the ordinary pressure sintering BN Plastic solid of high intensity is not acquired. On the other hand, if it exceeds 2100 degrees C, alkaline-earth-metal borate will cause a pyrolysis and evaporation, and will lose the operation as an original additive. It is a 1600-2100 degrees C [from which the ordinary pressure sintering BN Plastic solid of high intensity is acquired] non-oxidizing atmosphere especially desirably. As a non-oxidizing atmosphere, the inert atmosphere of helium, Ar, and N₂ grade is suitable. As baking equipment, a Tamman electric furnace, a resistance heating furnace, a high-frequency furnace, etc. are used.

The ordinary pressure sintering BN Plastic solid of this invention manufactured as mentioned above contains 98 - 96 % of the weight of BN(s), and 2 - 40 % of the weight of alkaline-earth-metal borate. When advanced electric insulation and thermal conductivity are required especially, 98 - 80 % of the weight of BN(s) and 2 - 20 % of the weight of alkaline-earth-metal borate are desirable. The content of alkaline-earth-metal borate does not become being less than 2 % of the weight with the sintered compact of high density and high intensity. On the other hand, if it exceeds 40 % of the weight, the property which was excellent in BN(s), such as thermal

conductivity and electric insulation, will fall remarkably. If especially the service temperature of a Plastic solid rises, this inclination will become much more intense. Moreover, the sintered compact consistency of the ordinary pressure sintering BN Plastic solid of this invention manufactured as mentioned above serves as bending strength of 550kg/cm² or more at 65 - 80% with relative density. At less than 65%, since there is much pore and it is not precise, bending strength and thermal conductivity of relative density do not improve, and it is not suitable for applications, such as a breaking ring and a heat sink. Moreover, if relative density surpasses 80%, machinability will fall.

<Example> Although this invention is explained to an example list still more concretely with the example of a comparison below, this invention is not limited to these.

Example 1 After adding CaO and the B-2O₃ 15 weight section in the commercial BN powder (hexagonal, 99.0% [of purity], and specific-surface-area 6m²/g) 85 weight section, it mixed with the ball mill, and the mixed powder for shaping was obtained. Next, isotropic pressure shaping between the colds of this mixed powder was carried out by the pressure of 5 ton/cm². The acquired preforming object was embedded into the graphite container containing said BN powder, and was calcinated in 1900 degrees C and 60 minutes and under Ar ambient atmosphere with the high-frequency furnace. The measurement result of the presentation of obtained BN sintered compact, relative density, insulation resistance, and thermal conductivity is shown in a table.

Example 2 It carried out by the same approach as an example 1 except having made compacting pressure into 7 ton/cm² using the mixed powder for shaping obtained in the example 1.

Example 3 In the BN powder 90 weight section used in the example 1, MgO·CaO and the 2B2O3·10 weight section were added and mixed, and the mixed powder for shaping was obtained. It carried out by the same approach as an example 1 using this powder except having made burning temperature into 1700 degrees C.

Example 4 Boric acid and a melamine were mixed by the weight ratio of 1:1, in the ammonia gas air current, it heat-treated and 1200 degrees C of BN powder of 90% of BN purity and specific-surface-area of 50m²/g were obtained for 4 hours. As a result of carrying out the X diffraction of this powder, it turned out that it is an amorphous substance BN. After carrying out 2CaO(s) and B-2O₃ 10 weight section addition at this powder 90 weight section, it mixed at the ball mill and the mixed powder for shaping was obtained. Compacting pressure was carried out by the same approach as an example 1 using this mixed powder except having made 7 ton/cm² and burning temperature into 1700 degrees C.

Example 5 After grinding BN powder used in the example 1 in atmospheric air until specific surface area was set to 80m²/g with the RAIKAI machine, washing desiccation was carried out with the methanol and BN impalpable powder was obtained. Specific surface area was measured with the BET adsorption method. CaO and B-2 O₃ were mixed with the ball mill in it, after adding 5 weight sections in this powder 95 weight section, and the mixed powder for shaping was obtained. Next, metal mold was filled up with this mixed powder, and 1 shaft pressing was carried out by the pressure of 2 ton/cm². It carried out by the same approach as an example 1 except having used this preforming object.

Example 6 In the BN impalpable powder 80 weight section obtained in the example 5, CaO-BaO and the 2B2O3·20 weight section were added and mixed, and the mixed powder for shaping was obtained. It carried out by the same approach as an example 1 except having used this mixed powder.

Example 7 BN powder used in the example 1 was ground under N₂ ambient atmosphere until specific surface area was set to 70m²/g by attritor, and BN impalpable powder was obtained. It carried out by the same approach as an example 5 except having used this powder.

Example 8 After grinding in atmospheric air until specific surface area was set to 60m²/g with the RAIKAI machine, after adding CaO and the B-2O₃ 15 weight section in the BN powder 85 weight section used in the example 1, washing desiccation was carried out with the methanol and the mixed powder for shaping was obtained. It carried out by the same approach as an example 5 except having used this mixed powder.

Example 9 It carried out by the same approach as an example 1 except having used the mixed powder for shaping obtained in the example 8.

Example 10 It ground under N₂ ambient atmosphere and the mixed powder for shaping was obtained after adding MgO-CaO and the 2B₂O₃2O weight section in the BN powder 80 weight section used in the example 1 until specific surface area was set to 70m²/g by attritor. It carried out by the same approach as an example 5 using this mixed powder except having made burning temperature into 1600 degrees C.

Example 1 of a comparison It carried out by the same approach as an example 1 except having used BN powder used in the example 1 as powder for shaping as it was.

Example 2 of a comparison It carried out by the same approach as an example 1 using the mixed powder for shaping obtained in the example 3 except having made compacting pressure into 2 ton/cm².

Example 3 of a comparison After carrying out 5 weight sections addition of B-2 O₃ at the BN powder 95 weight section used in the example 1, it mixed with the ball mill and the mixed powder for shaping was obtained. The example was carried out by the same approach as an example 5 except having used this mixed powder.

Example 4 of a comparison After carrying out 45 weight sections addition of CaO and 2B₂O₃ at the BN powder 55 weight section used in the example 1, it mixed with the ball mill and the mixed powder for shaping was obtained. It carried out by the same approach as an example 1 except having used this mixed powder.

In addition, physical-properties measurement of BN sintered compact indicated to the table was performed by the following approach.

(1) Relative density; from the dimension of a sintered compact, after asking for a consistency from the weight in quest of the volume, it computed by the relative density (%) = consistency (g/cm²) / theoretical density (g/cm²) x100.

(2) Based on JIS R-1601, it measured in cold bending strength.

(3) Insulation resistance; the obtained sintered compact was processed into the with an outer-diameter thickness [1mm thickness of 20mm] configuration, and the insulation resistance (omega) after 24hr preservation / moisture absorption was measured in the desiccator after processing and (NH₄) containing 2SO₄ solution.

(4) Thermal conductivity; It is based on a laser flash method.

種別	アルカリ土類金属硼酸塩		相対密度 (%)	曲げ強さ (kg/cm ²)	絶縁抵抗(Ω)		熱伝導率 (cal/cm, sec, °C)
	種類	含有量(%)			吸湿前	吸湿後	
実施例 1	CaO · B ₂ O ₃	15	74	550	10 ¹⁰	10 ¹¹	0.05
// 2	CaO · B ₂ O ₃	15	78	680	10 ¹⁰	10 ¹⁰	0.08
// 3	MgO · CaO · 2B ₂ O ₃	10	73	620	10 ¹⁰	10 ¹⁰	0.05
// 4	2CaO · B ₂ O ₃	10	80	940	10 ¹⁰	10 ¹⁰	0.10
// 5	CaO · B ₂ O ₃	5	68	580	10 ¹⁰	10 ¹⁰	0.09
// 6	CaO · BaO · 2B ₂ O ₃	20	77	980	10 ¹¹	10 ¹⁰	0.07
// 7	CaO · B ₂ O ₃	5	72	750	10 ¹⁰	10 ¹⁰	0.05
// 8	CaO · B ₂ O ₃	15	69	600	10 ¹⁰	10 ¹¹	0.04
// 9	CaO · B ₂ O ₃	15	77	950	10 ¹⁰	10 ¹⁰	0.08
// 10	MgO · CaO · 2B ₂ O ₃	20	75	800	10 ¹¹	10 ¹¹	0.05
比較例 1	—	—	75	180	10 ¹¹	10 ¹⁰	サンプル加工時破壊
// 2	MgO · CaO · 2B ₂ O ₃	10	63	320	10 ¹¹	10 ¹⁰	0.04
// 3	B ₂ O ₃	5	60	280	10 ⁹	10 ⁹	0.02
// 4	CaO · 2B ₂ O ₃	45	59	340	10 ⁹	10 ⁹	0.009

<Effect of the invention> The ordinary pressure sintering BN Plastic solid of this invention has the outstanding property which BN(s), such as electric insulation, thermal conductivity, corrosion resistance, and thermal shock resistance, have, and does not receive configuration constraint.

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(56) 参考文献 特開 昭 62-123070 (J P, A)

特開 昭 62-265175 (J P, A)

特開 昭 63-40769 (J P, A)

特開 昭 63-45174 (J P, A)

(54) 【発明の名称】 常圧焼結窒化硼素成形体

(57) 【特許請求の範囲】

【請求項 1】 アルカリ土類金属硼酸塩を 2~40 重量% 含有してなり、相対密度 65~80%、曲げ強さ 550kg/cm² 以上であることを特徴とする、絶縁抵抗 10¹⁰ Ω 以上、熱伝導率 0.04cal/cm・sec・℃ 以上の常圧焼結窒化硼素成形体。

【発明の詳細な説明】

<産業上の利用分野>

本発明は、常圧焼結窒化硼素成形体に関する。

<従来の技術>

窒化硼素 (BN) は、電気絶縁性、熱伝導性、耐食性、耐熱衝撃性、潤滑性等の優れた特性を有する一方、機械加工の容易な数少ないセラミックスである。このため上記諸特性が要求される金属溶融用の各種容器をはじめ、電気絶縁材料、高温伝熱材料等に広く利用されている。

BN 焼結体は、BN が難焼結性であるので一般にはホットプレス (加圧焼結) 法によって作られている。それは、1500~2300℃ にて 100kg/cm² を超える圧力をかけて実施するものであるため、大型形状品は得られず、また複雑形状品の製法には適さない等の問題がある。しかも、現在市販されている BN 成形体は、一旦、円柱状にホットプレスされた焼結体を機械加工して最終製品形状に仕上げる方法がとられているので高価格である。

10 以上のような問題を解決するため各種の常圧焼結法が試みられているが、現在までのところ、BN の特性の発揮できる BN 焼結体は得られていない。例えば、特開昭 61-132583 号公報では、高压ラバープレス成形し得られた予備成形体を黒鉛モールドに挿入して自由膨張を制限する下での焼結が試みられているのが、密度・強度が低い上、生産能率が悪く、大型形状品が得られない問題があ

る。そのため、電気絶縁性、熱伝導性、耐食性、耐熱衝撃性等のBN本来の優れた特性を有し、安価に、容易にかつ効率良く製造できる常圧焼結BN成形体の提供が望まれていた。

<発明が解決しようとする問題点>

本発明は、BN焼結体の形状制約と生産性を改善し従来得られなかった熱伝導性、電気絶縁性の良好な常圧焼結BN成形体を提供することを目的とするものである。

<問題点を解決するための手段>

すなわち、本発明は、アルカリ土類金属硼酸塩を2～40重量%含有してなり、相対密度65～80%、曲げ強さ550kg/cm²以上であることを特徴とする、絶縁抵抗10¹²Ω以上、熱伝導率0.04cal/cm・sec・℃以上の常圧焼結窒化硼素成形体である。

以下本発明を詳細に説明する。

本発明で用いるBN粉末は、市販品で良いが望ましくは、結晶性の高い六方晶のBN粉末である。この粉末は予備成形時の可塑性に優れているため高密度の予備成形体を得られ易い。アルカリ土類金属硼酸塩のアルカリ土類金属としては、マグネシウム、カルシウム、ストロ
ンチウム、バリウムの1種以上を任意に選択する。

本発明の成形体は、以上のBN粉末とアルカリ土類金属硼酸塩とを最終製品組成になるように混合された混合粉末を5ton/cm²以上の圧力にて成形した後焼成する方法、及び比表面積を入手したその2倍以上になるまで微粉砕してなるBN粉末にアルカリ土類金属硼酸塩を混合するか又はBNとアルカリ土類金属硼酸塩との混合物を比表面積が元の2倍以上になるまで破断、せん断、磨砕等の粉砕をした後2ton/cm²以上の圧力で成形した後焼成する方法によって製造することができる。

成形装置としては、金型成形機、冷間等方圧成形機(CIP)等の通常の成形機を用いることができる。結晶性の高い六方晶のBN粉末あるいは非晶質のBN粉末をそのまま用いる時の成形圧力は、5ton/cm²以上好ましくは7ton/cm²以上である。5ton/cm²未満の成形圧力では、相対密度65%以上の常圧焼結BN成形体を得ることが困難となる。一方、微粉砕したBN粉末あるいは入手した原料を混合して微粉砕した粉末を用いる時の成形圧力は、2ton/cm²以上で上記と同様の効果が得られる。この時の粉砕装置としては、ボールミル、振動ボールミル、アトライター、ライカイ機等の通常の粉砕機を用いることができる。なお、粉砕は、元の粉末の比表面積の2倍以上好ましくは10倍以上になるまで行う。2倍未満の粉砕では相対密度65%以上の常圧焼結BN成形体を得ることが困難となる。

粉砕を行う場合、それを酸化雰囲気で行うと硼素酸化物の生成がみられ、そのまま焼成すると焼結体中に遊離の酸化硼素が存在する状態となり耐湿性及び熱伝導率の低下をきたすばかりでなく、焼結体にクラックが発生する。この場合、生成した硼素酸化物を除去する処理を行

うことにより本発明品を得る原料として使用できる。硼素酸化物を除去する方法としては、メタノール、エタノール、グリセリン等のアルコール類による処理である。具体的には、アルコールを含んだスラリーの加熱あるいはアルコールにりよる洗浄・濾過である。粉砕を硼素酸化物が生成しないような例えばN₂、Ar等の非酸化性雰囲気で行えば上記の硼素酸化物を除去する工夫は必ずしも必要でない。

上記した方法により粉砕を行ったものは、高压成形をすることなく相対密度65%以上の常圧焼結BN成形体を得ることができる。これは、結晶の格子不整及び部分的な非晶質化が進むと同時に新たに形成された粒子面が現われ所謂メカノケミカル効果により活性化された粉末となったためと考えられる。高強度の常圧焼結BN成形体を得るには、成形圧力を高くして予備成形体密度をできるだけ高くすることが望ましい。

焼成は、1400～2100℃の非酸化性雰囲気で行う。焼成温度が1400℃未満では、BN粒同志及びBN粒とアルカリ土類金属硼酸塩が直接接合しにくいので高強度の常圧焼結BN成形体を得られない。一方、2100℃を超えるとアルカリ土類金属硼酸塩が熱分解・蒸発を起し本来の添加剤としての作用を失う。望ましくは、特に高強度の常圧焼結BN成形体を得られる1600～2100℃での非酸化性雰囲気である。非酸化性雰囲気としてはHe、Ar、N₂等の不活性雰囲気が適当である。焼成装置として、タンマン炉、抵抗加熱炉、高周波炉等が用いられる。

以上のようにして製造された本発明の常圧焼結BN成形体は、BN98～96重量%、アルカリ土類金属硼酸塩2～40重量%を含有する。特に高度の電気絶縁性、熱伝導性が要求される場合には、BN98～80重量%、アルカリ土類金属硼酸塩2～20重量%が好ましい。アルカリ土類金属硼酸塩の含有量が2重量%未満であると、高密度、高強度の焼結体とはならない。一方、40重量%を超えると、熱伝導性、電気絶縁性等のBNの優れた特性が著しく低下する。特に成形体の使用温度が上昇するとこの傾向は一層激しくなる。また、以上のようにして製造された本発明の常圧焼結BN成形体の焼結体密度は、相対密度で65～80%で曲げ強さ550kg/cm²以上となる。相対密度が65%未満では気孔が多く緻密でないため、曲げ強さ及び熱伝導性が向上せず、ブレーキング、放熱板等の用途には適さない。また、相対密度が80%をこえると機械加工性が低下する。

<実施例>

以下本発明を実施例並びに比較例をもってさらに具体的に説明するが、本発明はこれらに限定されるものではない。

実施例1

市販のBN粉末(六方晶、純度99.0%、比表面積6m²/g)85重量部にCaO・B₂O₃15重量部を添加した後ボールミルにて混合し、成形用混合粉末を得た。次にこの混合粉

末を 5ton/cm^2 の圧力で冷間等方圧成形した。得られた予備成形体を前記BN粉末の入った黒鉛容器中に埋め込み高周波炉にて 1900°C 、80分間、 Ar 雰囲気下で焼成した。得られたBN焼結体の組成、相対密度、絶縁抵抗、熱伝導率の測定結果を表に示す。

実施例 2

実施例 1 で得た成形用混合粉末を用い成形圧力を 7ton/cm^2 としたこと以外は実施例 1 と同様の方法にて実施した。

実施例 3

実施例 1 で用いたBN粉末90重量部に $\text{MgO} \cdot \text{CaO} \cdot 2\text{B}_2\text{O}_3$ 10重量部を添加・混合して成形用混合粉末を得た。この粉末を用い、焼成温度を 1700°C としたこと以外は、実施例 1 と同様の方法により実施した。

実施例 4

硝酸とメラミンとを1:1の重量比率で混合しアンモニアガス気流中にて 1200°C 、4時間、加熱処理してBN純度90%、比表面積 $50\text{m}^2/\text{g}$ のBN粉末を得た。この粉末をX線回折した結果、非晶質BNであることが判った。この粉末90重量部に $2\text{CaO} \cdot \text{B}_2\text{O}_3$ 10重量部添加した後ボールミールにて混合し成形用混合粉末を得た。この混合粉末を用い、成形圧力を 7ton/cm^2 及び焼成温度を 1700°C としたこと以外は実施例 1 と同様の方法にて実施した。

実施例 5

実施例 1 で用いたBN粉末をライカイ機で比表面積が $60\text{m}^2/\text{g}$ になるまで大気中にて粉碎した後、メタノールで洗浄乾燥しBN微粉末を得た。比表面積は、BET法にて測定した。この粉末95重量部に $\text{CaO} \cdot \text{B}_2\text{O}_3$ を5重量部を添加した後ボールミールにて混合し成形用混合粉末を得た。次に該混合粉末を金型に充填し 2ton/cm^2 の圧力で一軸加圧成形した。この予備成形体を用いたこと以外は実施例 1 と同様の方法にて実施した。

実施例 6

実施例 5 で得たBN微粉末80重量部に $\text{CaO} \cdot \text{BaO} \cdot 2\text{B}_2\text{O}_3$ 20重量部を添加・混合して成形用混合粉末を得た。この混合粉末を用いたこと以外は実施例 1 と同様の方法にて実施した。

実施例 7

実施例 1 で用いたBN粉末をアトライターで比表面積が $70\text{m}^2/\text{g}$ になるまで N_2 雰囲気下にて粉碎しBN微粉末を得た。この粉末を用いたこと以外は、実施例 5 と同様の方法にて実施した。

実施例 8

実施例 1 で用いたBN粉末85重量部に $\text{CaO} \cdot \text{B}_2\text{O}_3$ 15重量

部を添加した後、ライカイ機で比表面積が $60\text{m}^2/\text{g}$ になるまで大気中にて粉碎した後、メタノールで洗浄乾燥し成形用混合粉末を得た。この混合粉末を用いたこと以外は、実施例 5 と同様の方法にて実施した。

実施例 9

実施例 8 で得た成形用混合粉末を用いたこと以外は実施例 1 と同様の方法にて実施した。

実施例 10

実施例 1 で用いたBN粉末80重量部に $\text{MgO} \cdot \text{CaO} \cdot 2\text{B}_2\text{O}_3$ 20重量部を添加した後、アトライターで比表面積が $70\text{m}^2/\text{g}$ になるまで N_2 雰囲気下にて粉碎し成形用混合粉末を得た。この混合粉末を用い、焼成温度を 1600°C としたこと以外は、実施例 5 と同様の方法にて実施した。

比較例 1

実施例 1 で用いたBN粉末をそのまま成形用の粉末として用いたこと以外は実施例 1 と同様の方法により実施した。

比較例 2

実施例 3 で得た成形用混合粉末を用い、成形圧力を 2ton/cm^2 としたこと以外は実施例 1 と同様の方法にて実施した。

比較例 3

実施例 1 で用いたBN粉末95重量部に B_2O_3 を5重量部添加した後ボールミールで混合し成形用混合粉末を得た。この混合粉末を用いたこと以外は実施例 5 と同様の方法にて実施した。

比較例 4

実施例 1 で用いたBN粉末55重量部に $\text{CaO} \cdot 2\text{B}_2\text{O}_3$ を45重量部添加した後ボールミールで混合し成形用混合粉末を得た。この混合粉末を用いたこと以外は実施例 1 と同様の方法により実施した。

尚、表に記載したBN焼結体の物性測定は次の方法により行った。

(1) 相対密度：焼結体の寸法より体積を求めその重量より密度を求めた後、相対密度(%) = 密度(g/cm^3) / 理論密度(g/cm^3) $\times 100$ で算出した。

(2) 常温曲げ強さ：JIS R-1601に準拠して測定した。

(3) 絶縁抵抗：得られた焼結体を外径 20mm 厚み 1mm の形状に加工し、加工後及び $(\text{NH}_4)_2\text{SO}_4$ 溶液の入ったデシケータ中に24hr保存・吸湿後の絶縁抵抗(Ω)を測定した。

(4) 熱伝導率：レーザーフラッシュ法による。

種別	アルカリ土類金属硼酸塩		相対密度 (%)	曲げ強さ (kg/cm)	絶縁抵抗(Ω)		熱伝導率 (cal/cm.sec. $^{\circ}\text{C}$)
	種類	含有量(%)			吸湿前	吸湿後	
実施例 1	$\text{CaO} \cdot \text{B}_2\text{O}_3$	15	74	550	10^{12}	10^{11}	0.05
// 2	$\text{CaO} \cdot \text{B}_2\text{O}_3$	15	78	680	10^{12}	10^{12}	0.08
// 3	$\text{MgO} \cdot \text{CaO} \cdot 2\text{B}_2\text{O}_3$	10	73	620	10^{12}	10^{12}	0.05
// 4	$2\text{CaO} \cdot \text{B}_2\text{O}_3$	10	80	940	10^{12}	10^{12}	0.10
// 5	$\text{CaO} \cdot \text{B}_2\text{O}_3$	5	68	580	10^{12}	10^{12}	0.09
// 6	$\text{CaO} \cdot \text{BaO} \cdot 2\text{B}_2\text{O}_3$	20	77	980	10^{11}	10^{10}	0.07
// 7	$\text{CaO} \cdot \text{B}_2\text{O}_3$	5	72	750	10^{12}	10^{12}	0.05
// 8	$\text{CaO} \cdot \text{B}_2\text{O}_3$	15	69	800	10^{12}	10^{11}	0.04
// 9	$\text{CaO} \cdot \text{B}_2\text{O}_3$	15	77	950	10^{12}	10^{12}	0.06
// 10	$\text{MgO} \cdot \text{CaO} \cdot 2\text{B}_2\text{O}_3$	20	75	900	10^{11}	10^{11}	0.05
比較例 1	—	—	75	180	10^{11}	10^{10}	サンプル加工時破壊
// 2	$\text{MgO} \cdot \text{CaO} \cdot 2\text{B}_2\text{O}_3$	10	63	320	10^{11}	10^{10}	0.04
// 3	B_2O_3	5	60	280	10^9	10^9	0.02
// 4	$\text{CaO} \cdot 2\text{B}_2\text{O}_3$	45	59	340	10^9	10^9	0.009

<発明の効果>

性、耐食性、耐熱衝撃性等のBNの持つ優れた特性を有
 本発明の常圧焼結BN成形体は、電気絶縁性、熱伝導 20 し、形状制約を受けることがない。